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DECLARATION

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I, Paul David Churchill Clarke, BA. MITI., translator to Taylor & Meyer of 20 Kingsmead Road, London SW2 3JD, England, do solemnly and sincerely declare as follows:

1. That I am well acquainted with the English and German languages;
2. That the following is a true translation made by me into the English language of German Patent Application No. 100 37 765.3;
3. That all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardise the validity of the application or any patent issued thereon.

Signed, this 12 day of December 2002

  
Harrogate, HG1 4QD, England

# FEDERAL REPUBLIC OF GERMANY

## Certificate of Priority for Filing of a Patent Application

**Filing number:** 100 37 765.3

**Filing date:** 3rd August 2000

**Applicant/Proprietor:** Agfa-Gevaert AG, Leverkusen/  
Germany

**Title:** A bleach-fixing agent bath  
concentrate

**Priority:** 27.5.2000 DE 100 26 456.5

**IPC:** G 03 C 5/38

The attached papers are a true and accurate reproduction of  
the original documents for this patent application.

Munich, 22nd October 2002

On behalf of the President  
of the German Patent and Trade  
Mark Office

(signature)

Agurks

**A bleach-fixing agent bath concentrate**

This invention relates to a one-part bleach-fixing agent bath concentrate (BX concentrate) with which bleach-fixing agent baths can be made up or regenerated.

5

BX baths are used in colour photographic processing in order to oxidise the metallic silver formed by development into a soluble form thereof (bleaching) and in order to dissolve it in this form, together with undeveloped silver halide, from the material by complexation (fixing). For these purposes, BX baths contain a series of necessary chemicals, namely an iron(III) complex salt as an oxidant, a thiosulfate as a fixing agent, and a sulfite, a disulfite or a sulfinic acid as a stabiliser for the thiosulfate. These chemicals exert an effect on each other, so that they cannot be held for an extended period in the same solution. For example, the iron(III) complex salt oxidises the sulfite, the disulfite or the sulfinic acid. The thiosulfate is thereby no longer stabilised, so that it then decomposes.

15

For this reason, BX baths are produced as two or three parts which are not combined with each other until just before they are used. Concentrates which are required for regeneration, i.e. for replenishing chemicals which have been consumed, are likewise formulated as two or three parts.

20

Multi-part formulation of the constituents of a BX tank bath or of a BX regenerator is disadvantageous, firstly because it is costly and uneconomic, and secondly because it results, time after time, in errors of addition.

25

There is therefore a great need for the chemicals for BX baths to be formulated as one part, and in particular there is a need to provide a one-part BX concentrate which can be converted very easily, namely by dilution with water, into a ready-to-use BX bath, or which can be used just as easily for regenerating a BX bath. Attempts to satisfy these needs have hitherto failed because of the aforementioned decomposition of the thiosulfate, and also due to insufficient solubility of the

30

thiosulfate, of the sulfite and of the iron(III) complex salt, particularly if the latter is iron(III)-EDTA.

Surprisingly, it has now been found that these disadvantages can be overcome if a phosphate, polyphosphate or polyphosphonate, or a nitrate or bromide, is added to the BX concentrate containing the aforementioned constituents.

Complex salts of Fe(III) which are suitable for photographic bleach and bleach-fixing baths are known from numerous documents (e.g. EP 329 088, 584 665, 507 126, 556 782, 532 003, 750 226, 657 777, 599 620, 588 289, 723 194, 851 287, 840 168, 871 065, 567 126, 726 203 and US 5 670 305).

The preferred complexing agents for Fe(III) are: ethylenediaminetetraacetic acid (EDTA), propylenediaminetetraacetic acid (PDTA),  $\beta$ -alaninediacetic acid (ADA), diethylenetriaminepentaacetic acid (DTPA), methyliminodiacetic acid (MIDA), ethylenediamine monosuccinate (EDMS), methylglycinediacetic acid (MGDA), ethylenediamine disuccinate (EDDS), particularly (S,S)-EDDS, iminosuccinic acid, iminosuccinic acid-propionic acid, and 2-hydroxypropyliminodiacetic acid.

Mixtures of complexing agents can also be used.

Examples of suitable sulfites include ammonium sulfite, ammonium hydrogen sulfite, sodium sulfite, sodium disulfite, sodium hydrogen sulfite, potassium sulfite, potassium disulfite and potassium hydrogen sulfite. Examples of suitable sulfinic acids include hydroxymethanesulfinic acid, formamidinesulfinic acid, benzenesulfinic acid, p-toluenesulfinic acid, methanesulfinic acid, o-amidosulfinic acid and salts thereof.

Alkali salts and/or ammonium salts can be used as phosphates, e.g. ammonium dihydrogen phosphate, diammonium hydrogen phosphate, triammonium phosphate, potassium dihydrogen phosphate, dipotassium hydrogen phosphate, tripotassium

phosphate, sodium dihydrogen phosphate, disodium hydrogen phosphate, and trisodium phosphate.

5 Examples of polyphosphates and polyphosphonates which can be used include sodium hexametaphosphate, sodium tetrphosphate, hydroxyethanediphosphonic acid, N(-2-carboxyethyl)-1-aminoethane-1,1-diphosphonic acid, N,N-bis-(carboxymethylene)-1-aminoethane-1,1-diphosphonic acid, morpholinomethane-diphosphonic acid, nitrilotrismethylene-phosphonic acid, ethylenediamine-tetramethylene phosphonic acid, hexamethylenediaminetetramethylene phosphonic  
10 acid, 2-phosponobutane-1,2,4-tricarboxylic acid, and 2-carboxyethane-phosphonic acid. Free polyphosphoric acids are also suitable.

Alkali and/or ammonium nitrates and bromides can be used as nitrates and bromides.

15 The phosphates, polyphosphates and polyphosphonates, nitrates and bromides are preferably added to the concentrate in an amount ranging from 0.01 to 2.5 mol/litre, particularly from 0.05 to 1 mol/litre.

20 Sodium, potassium and ammonium thiosulfates are particularly suitable as fixing agents.

Other constituents can include aminopolycarboxylic acid, rehalogenating agents, acids and alkalies for pH adjustment, bleaching accelerators, white couplers and  
25 buffer substances (see Research Disclosure 37 038, February 1995, pages 107 to 109).

In particular, the pH ranges from 4 to 9.

30 In addition, other complexing agents can also be added, individually or in admixture.

Polycarboxylic acids: e.g. oxalic acid, malonic acid, glutaric acid, adipic acid, suberic acid, fumaric acid, maleic acid, itaconic acid;

5 (Poly)hydroxypolycarboxylic acids: e.g. citric acid, glycolic acid, lactic acid, malic acid, tartaric acid, galactaric acid.

**Examples****Example 1**

5 1 litre of BX concentrate contains

|   |           |
|---|-----------|
| ammonium thiosulfate solution, 57% by weight        | 400 ml    |
| ammonium hydrogen sulfite solution, 66% by weight   | 80 ml     |
| NH <sub>4</sub> Fe(III)EDTA solution, 48% by weight | 330 ml    |
| additives   | see below |
| pH  | 5.5       |

The pH is adjusted with NH<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub>.

15 The following additions were made to the BX concentrates: BX 1: no additives

BX 2: 40 g/l sodium acetate (0.49 mol/litre)

BX 3: 186 g/l trisodium phosphate dodecahydrate (0.49 mol/litre)

BX 4: 50 g/l sodium hexametaphosphate (0.082 mol/litre)

20 BX 5: 73 ml/l aminotrismethylene-phosphonic acid, concentration 50% by weight  
(0.16 mol/litre)

| Storage at 60°C     | Sodium sulfite content [g/l] |      |      |      |      |
|---------------------|------------------------------|------|------|------|------|
| Duration of storage | BX 1                         | BX 2 | BX 3 | BX 4 | BX 5 |
| No storage          | 82.7                         | 82.5 | 82.4 | 82.6 | 82.3 |
| 2 days              | 55.6                         | 56.0 | 65.4 | 64.9 | 65.1 |
| 6 days              | Precipitates of sulfur       |      | 54.0 | 54.2 | 53.8 |

The stability of the sulfite is considerably improved by the addition of phosphate, polyphosphate and polyphosphonate.

25

The BX concentrate according to the invention can be used without disadvantages instead of a conventional, two-part BX concentrate, for example in the standard AP

94 process for the bleach-fixing of exposed, developed colour paper based on chloride-rich silver halide emulsions.

### **Example 2**

5

The following additions were made to a BX concentrate as in Example 1 (no additives):

BX 1: no additives

BX 2: 40 g/l sodium acetate (0.49 mol/litre)

10 BX 3: 48.5 g/l ammonium dihydrogen phosphate (0.49 mol/litre)

BX 4: 48 g/l ammonium bromide (0.49 mol/litre)

BX 5: 73 ml/l ammonium nitrate (0.49 mol/litre)

| <b>BX concentrate</b> | <b>Formation of crystals after 5 days at -5°C</b> |
|-----------------------|---|
| BX 1                  | crystals  |
| BX 2                  | crystals  |
| BX 3                  | no crystals                                       |
| BX 4                  | no crystals                                       |
| BX 5                  | no crystals                                       |

15 The addition of phosphate, bromide or nitrate prevents the formation of crystals in a one-part bleach-fixing agent bath concentrate, so that a stable concentrate which comprises contents of active ingredients which would otherwise not be possible can also be produced.

20 The BX concentrate according to the invention is particularly suitable for short processing times (CD and BX times ranging from 12 to 35 seconds) and for a colour developer (CD) which contains disulfoethylhydroxylamine (HADS) as an antioxidant.



**Claims**

1. A one-part photographic bleach-fixing agent bath concentrate containing an iron(III) complex salt, a thiosulfate and a sulfite, a disulfite or a sulfinic acid,  
5 characterised in that it additionally contains a phosphate, polyphosphate or polyphosphonate, or a nitrate or bromide.
2. A one-part bleach-fixing agent bath concentrate according to claim 1,  
10 characterised in that its content of thiosulfate is 0.5 to 25 mol/litre, its content of sulfite is 0.2 to 2 mol/litre and its content of Fe(III) complex salt is 0.1 to 1 mol/litre.
3. A one-part bleach-fixing agent bath concentrate according to claims 1 or 2,  
15 characterised in that its pH is 4 to 9.
4. A one-part bleach-fixing agent bath concentrate according to claims 1 or 2,  
characterised in that its pH is 5 to 6.5.
5. A one-part bleach-fixing agent bath concentrate according to any of claims 1  
20 to 4, characterised in that the amount of phosphate, nitrate or bromide is 0.01 to 2.5 mol/litre.
6. A one-part bleach-fixing agent bath concentrate according to any of claims 1  
25 to 5, characterised in that it additionally contains one or more complexing agents.
7. A one-part photographic bleach-fixing agent bath concentrate containing an  
30 iron(III) complex salt, a thiosulfate, and a sulfite or a sulfinic acid, characterised in that it additionally contains a phosphate, polyphosphate or polyphosphonate.

**A bleach-fixing agent bath concentrate**

**Abstract**

A one-part photographic bleach-fixing agent bath concentrate containing an iron(III) complex salt, a thiosulfate and a sulfite, a disulfite or a sulfinic acid, remains stable if a phosphate, polyphosphate or polyphosphonate, or a nitrate or bromide is added thereto.



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2. That the following is a true translation made by me into the English language of German Patent Application No. 100 39 719.0;
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Signed, this 12 day of December 2002

P.D.C. Clarke.

Harrogate, HG1 4QD, England

# FEDERAL REPUBLIC OF GERMANY



## Certificate of Priority for Filing of a Patent Application

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DEC 31 2002  
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**Filing number:** 100 39 719.0

**Filing date:** 14th August 2000

**Applicant/Proprietor:** Agfa-Gevaert Aktiengesellschaft,  
Leverkusen/Germany

**Title:** A bleach-fixing agent bath  
concentrate

**Priority:** 27.05.2000 DE 100 26 456.5  
03.08.2000 DE 100 37 765.3

**IPC:** G 03 C 5/38

The attached papers are a true and accurate reproduction of  
the original documents for this patent application.

Munich, 7th November 2002

On behalf of the President  
of the German Patent and Trade  
Mark Office

(signature)

Hoiß

**A bleach-fixing agent bath concentrate**

This invention relates to a one-part bleach-fixing agent bath concentrate (BX concentrate) with which bleach-fixing agent baths can be made up or regenerated,  
5 and also relates to a bleach-fixing agent bath.

BX baths are used in colour photographic processing in order to oxidise the metallic silver formed by development into a soluble form thereof (bleaching) and in order to dissolve it in this form, together with undeveloped silver halide, from the material  
10 by complexation (fixing). For these purposes, BX baths contain a series of necessary chemicals, namely an iron(III) complex salt as an oxidant, a thiosulfate as a fixing agent, and a sulfite, a disulfite or a sulfinic acid as a stabiliser for the thiosulfate. These chemicals exert an effect on each other, so that they cannot be held for an extended period in the same solution. For example, the iron(III) complex salt  
15 oxidises the sulfite, the disulfite or the sulfinic acid. The thiosulfate is thereby no longer stabilised, so that it then decomposes.

For this reason, BX baths are produced as two or three parts which are not combined with each other until just before they are used. Concentrates which are required for  
20 regeneration, i.e. for replenishing chemicals which have been consumed, are likewise formulated as two or three parts.

Multi-part formulation of the constituents of a BX tank bath or of a BX regenerator is disadvantageous, firstly because it is costly and uneconomic, and secondly  
25 because it results, time after time, in errors of addition.

There is therefore a great need for the chemicals for BX baths to be formulated as one part, and in particular there is a need to provide a one-part BX concentrate which can be converted very easily, namely by dilution with water, into a ready-to-  
30 use BX bath, or which can be used just as easily for regenerating a BX bath. Attempts to satisfy these needs have hitherto failed because of the aforementioned decomposition of the thiosulfate, and also due to insufficient solubility of the

thiosulfate, of the sulfite and of the iron(III) complex salt, particularly if the latter is iron(III)-EDTA.

Surprisingly, it has now been found that these disadvantages can be overcome if at least one compound from the series comprising a phosphate, polyphosphate or polyphosphonate, or a nitrate or bromide, is added to the BX concentrate containing the aforementioned constituents.

Complex salts of Fe(III) which are suitable for photographic bleach and bleach-fixing baths are known from numerous documents (e.g. EP 329 088, 584 665, 507 126, 556 782, 532 003, 750 226, 657 777, 599 620, 588 289, 723 194, 851 287, 840 168, 871 065, 567 126, 726 203 and US 5 670 305).

The preferred complexing agents for Fe(III) are: ethylenediaminetetraacetic acid (EDTA), propylenediaminetetraacetic acid (PDTA),  $\beta$ -alaninediacetic acid (ADA), diethylenetriaminepentaacetic acid (DTPA), methyliminodiacetic acid (MIDA), ethylenediamine monosuccinate (EDMS), methylglycinediacetic acid (MGDA), ethylenediamine disuccinate (EDDS), particularly (S,S)-EDDS, iminosuccinic acid, iminosuccinic acid-propionic acid, and 2-hydroxypropyliminodiacetic acid.

Mixtures of complexing agents can also be used.

Examples of suitable sulfites include ammonium sulfite, ammonium hydrogen sulfite, sodium sulfite, sodium disulfite, sodium hydrogen sulfite, potassium sulfite, potassium disulfite and potassium hydrogen sulfite. Examples of suitable sulfinic acids include hydroxymethanesulfinic acid, formamidinesulfinic acid, benzenesulfinic acid, p-toluenesulfinic acid, methanesulfinic acid, o-amidosulfinic acid and salts thereof.

Alkali salts and/or ammonium salts can be used as phosphates, e.g. ammonium dihydrogen phosphate, diammonium hydrogen phosphate, triammonium phosphate, potassium dihydrogen phosphate, dipotassium hydrogen phosphate, tripotassium

phosphate, sodium dihydrogen phosphate, disodium hydrogen phosphate, and trisodium phosphate.

5 Examples of polyphosphates and polyphosphonates which can be used include sodium hexametaphosphate, sodium tetrphosphate, hydroxyethanediphosphonic acid, N(-2-carboxyethyl)-1-aminoethane-1,1-diphosphonic acid, N,N-bis-(carboxymethylene)-1-aminoethane-1,1-diphosphonic acid, morpholinomethane-diphosphonic acid, nitrilotrismethylene-phosphonic acid, ethylenediamine-tetramethylene phosphonic acid, hexamethylenediaminetetramethylene phosphonic  
10 acid, 2-phosponobutane-1,2,4-tricarboxylic acid, and 2-carboxyethane-phosphonic acid. Free polyphosphoric acids are also suitable.

Alkali and/or ammonium nitrates and bromides can be used as nitrates and bromides.

15 The phosphates, polyphosphates and polyphosphonates, nitrates and bromides are preferably added to the concentrate in an amount ranging from 0.01 to 2.5 mol/litre, particularly from 0.05 to 1 mol/litre.

20 Sodium, potassium and ammonium thiosulfates are particularly suitable as fixing agents.

Other constituents can include aminopolycarboxylic acid, rehalogenating agents, acids and alkalies for pH adjustment, bleaching accelerators, white couplers and  
25 buffer substances (see Research Disclosure 37 038, February 1995, pages 107 to 109).

In particular, the pH ranges from 4 to 9.

30 In addition, other complexing agents can also be added, individually or in admixture.

Polycarboxylic acids: e.g. oxalic acid, malonic acid, glutaric acid, adipic acid, suberic acid, fumaric acid, maleic acid, itaconic acid;

(Poly)hydroxypolycarboxylic acids: e.g. citric acid, glycolic acid, lactic acid, malic acid, tartaric acid, galactaric acid.

5

The present invention further relates to a ready-to-use bleach-fixing agent bath of the type cited at the outset, which is characterised in that it additionally contains a phosphate, particularly in an amount from 0.01 to 0.6 mol/litre, and a polyphosphate, particularly in an amount from 0.5 to 50 mmol/litre.

10

The bleach-fixing agent bath can be produced from the concentrate according to the invention if the concentrate contains phosphate and/or polyphosphate.

15



**Examples****Example 1**

5 1 litre of BX concentrate contains

|   |           |
|---|-----------|
| ammonium thiosulfate solution, 57% by weight        | 400 ml    |
| ammonium hydrogen sulfite solution, 66% by weight   | 80 ml     |
| NH <sub>4</sub> Fe(III)EDTA solution, 48% by weight | 330 ml    |
| 10 additives  | see below |
| pH  | 5.5       |

The pH is adjusted with NH<sub>3</sub> or H<sub>2</sub>SO<sub>4</sub>.

15 The following additions were made to the BX concentrates:

BX 1: no additives

BX 2: 40 g/l sodium acetate (0.49 mol/litre)

BX 3: 186 g/l trisodium phosphate dodecahydrate (0.49 mol/litre)

BX 4: 50 g/l sodium hexametaphosphate (0.082 mol/litre)

20 BX 5: 73 ml/l aminotris(methylene)-phosphonic acid, concentration 50% by weight (0.16 mol/litre)

| Storage at 60°C     | Sodium sulfite content [g/l] |      |      |      |      |
|---------------------|------------------------------|------|------|------|------|
| Duration of storage | BX 1                         | BX 2 | BX 3 | BX 4 | BX 5 |
| No storage          | 82.7                         | 82.5 | 82.4 | 82.6 | 82.3 |
| 2 days              | 55.6                         | 56.0 | 65.4 | 64.9 | 65.1 |
| 6 days              | Precipitates of sulfur       |      | 54.0 | 54.2 | 53.8 |

25 The stability of the sulfite is considerably improved by the addition of phosphate, polyphosphate and polyphosphonate.

The BX concentrate according to the invention can be used without disadvantages instead of a conventional, two-part BX concentrate, for example in the standard AP 94 process for the bleach-fixing of exposed, developed colour paper based on chloride-rich silver halide emulsions.

5

**Example 2**

The following additions were made to a BX concentrate as in Example 1 (no additives):

10

BX 1: no additives

BX 2: 40 g/l sodium acetate (0.49 mol/litre)

BX 3: 48.5 g/l ammonium dihydrogen phosphate (0.49 mol/litre)

BX 4: 48 g/l ammonium bromide (0.49 mol/litre)

BX 5: 73 g/l ammonium nitrate (0.49 mol/litre)

15

| <b>BX concentrate</b> | <b>Formation of crystals after 5 days at -5°C</b> |
|-----------------------|---|
| BX 1                  | crystals  |
| BX 2                  | crystals  |
| BX 3                  | no crystals                                       |
| BX 4                  | no crystals                                       |
| BX 5                  | no crystals                                       |

20

The addition of phosphate, bromide or nitrate prevents the formation of crystals in a one-part bleach-fixing agent bath concentrate, so that a stable concentrate which comprises contents of active ingredients which would otherwise not be possible can also be produced.

25

The BX concentrate according to the invention is particularly suitable for short processing times (CD and BX times ranging from 12 to 35 seconds) and for a colour developer (CD) which contains disulfoethylhydroxylamine (HADS) as an antioxidant.

**Example 3**

A ready-to-use bleach-fixing agent bath was produced from the following components:

5

ammonium thiosulfate solution, 57% by weight 90 ml

sodium sulfite 10 g

NH<sub>4</sub> Fe(III)EDTA solution, 48 % by weight 70 ml

potassium dihydrogen phosphate 20 g

10

sodium hexametaphosphate 5 g

water to make up to 1 litre

Adjust pH to 6.5 with ammonia or phosphoric acid

15

This bleach-fixing agent bath is distinguished by the improved stability of the sulfite. It can be produced from a concentrate according to the invention.

**Claims**

1. A one-part photographic bleach-fixing agent bath concentrate containing an iron(III) complex salt, a thiosulfate and a sulfite, a disulfite or a sulfinic acid,  
5 characterised in that it additionally contains at least one compound from the series comprising a phosphate, polyphosphate or polyphosphonate, or a nitrate or bromide.
2. A one-part bleach-fixing agent bath concentrate according to claim 1,  
10 characterised in that its content of thiosulfate is 0.5 to 25 mol/litre, its content of sulfite is 0.2 to 2 mol/litre and its content of Fe(III) complex salt is 0.1 to 1 mol/litre.
3. A one-part bleach-fixing agent bath concentrate according to claims 1 or 2,  
15 characterised in that its pH is 4 to 9.
4. A one-part bleach-fixing agent bath concentrate according to claims 1 or 2, characterised in that its pH is 5 to 6.5.
- 20 5. A one-part bleach-fixing agent bath concentrate according to any of claims 1 to 4, characterised in that the amount of phosphate, polyphosphate, polyphosphonate, nitrate or bromide is 0.01 to 2.5 mol/litre.
- 25 6. A one-part bleach-fixing agent bath concentrate according to any of claims 1 to 5, characterised in that it additionally contains one or more complexing agents.
7. A one-part photographic bleach-fixing agent bath concentrate containing an iron(III) complex salt, a thiosulfate, and a sulfite or a sulfinic acid,  
30 characterised in that it additionally contains a phosphate, polyphosphate or polyphosphonate.

8. A ready-to-use bleach-fixing agent bath containing an iron(III) complex salt, a thiosulfate, and a sulfite, a disulfite or a sulfinic acid, characterised in that it additionally contains a phosphate and a polyphosphate.
- 5 9. A ready-to-use bleach-fixing agent bath according to claim 8, characterised in that the phosphate is contained in an amount from 0.01 to 0.6 mol and the polyphosphate is contained in an amount from 0.5 to 50 mmol per litre.
- 10 10. A ready-to-use bleach-fixing agent bath according to claims 8 and 9, characterised in that it is produced from a concentrate according to any of claims 1 to 7.

**A bleach-fixing agent bath concentrate**

**A b s t r a c t**

A one-part photographic bleach-fixing agent bath concentrate containing an iron(III) complex salt, a thiosulfate and a sulfite, a disulfite or a sulfinic acid, remains stable if a phosphate, polyphosphate or polyphosphonate, or a nitrate or bromide is added thereto.



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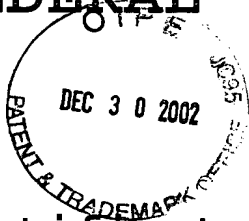
I, Paul David Churchill Clarke, BA. MITI., translator to Taylor & Meyer of 20 Kingsmead Road, London SW2 3JD, England, do solemnly and sincerely declare as follows:

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**Filing number:** 100 26 456.5

**Filing date:** 27th May 2000

**Applicant/Proprietor:** AGFA-GEVAERT AKTIENGESELLSCHAFT,  
Leverkusen/Germany

**Title:** A bleach-fixing agent bath  
concentrate

**IPC:** G 03 C 5/38

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(signature)

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10 necessary chemicals, namely an iron(III) complex salt as an oxidant, a thiosulfate as a fixing agent, and a sulfite, a disulfite or a sulfinic acid as a stabiliser for the thiosulfate. These chemicals exert an effect on each other, so that they cannot be held for an extended period in the same solution. For example, the iron(III) complex salt oxidises the sulfite, the disulfite or the sulfinic acid. The thiosulfate is thereby  
15 no longer stabilised, so that it then decomposes.

For this reason, BX baths are produced as two or three parts which are not combined with each other until just before they are used. Concentrates which are required for regeneration, i.e. for replenishing chemicals which have been consumed, are  
20 likewise formulated as two or three parts.

Multi-part formulation of the constituents of a BX tank bath or of a BX regenerator is disadvantageous, firstly because it is costly and uneconomic, and secondly because it results, time after time, in errors of addition.  
25

There is therefore a great need for the chemicals for BX baths to be formulated as one part, and in particular there is a need to provide a one-part BX concentrate which can be converted very easily, namely by dilution with water, into a ready-to-use BX bath, or which can be used just as easily for regenerating a BX bath.  
30

Surprisingly, it has now been found that said object can be achieved by adding a phosphate, polyphosphate or polyphosphonate to the BX concentrate containing the aforementioned constituents.

5      Complex salts of Fe(III) which are suitable for photographic bleach and bleach-fixing baths are known from numerous documents (e.g. EP 329 088, 584 665, 507 126, 556 782, 532 003, 750 226, 657 777, 599 620, 588 289, 723 194, 851 287, 840 168, 871 065, 567 126, 726 203 and US 5 670 305).

10     The preferred complexing agents for Fe(III) are: ethylenediaminetetraacetic acid (EDTA), propylenediaminetetraacetic acid (PDTA),  $\beta$ -alaninediacetic acid (ADA), diethylenetriaminepentaacetic acid (DTPA), methyliminodiacetic acid (MIDA), ethylenediamine monosuccinate (EDMS), methylglycinediacetic acid (MGDA),  
15     ethylenediamine disuccinate (EDDS), particularly (S,S)-EDDS, iminosuccinic acid, iminosuccinic acid-propionic acid, and 2-hydroxypropyliminodiacetic acid.

Mixtures of complexing agents can also be used.

20     Examples of suitable sulfites include ammonium sulfite, ammonium hydrogen sulfite, sodium sulfite, sodium disulfite, sodium hydrogen sulfite, potassium sulfite, potassium disulfite and potassium hydrogen sulfite. Examples of suitable sulfinic acids include hydroxymethanesulfinic acid, formamidinesulfinic acid, benzenesulfinic acid, p-toluenesulfinic acid, methanesulfinic acid, o-amidosulfinic acid and salts thereof.

25     Alkali salts and/or ammonium salts can be used as phosphates, e.g. ammonium dihydrogen phosphate, diammonium hydrogen phosphate, triammonium phosphate, potassium dihydrogen phosphate, dipotassium hydrogen phosphate, tripotassium phosphate, sodium dihydrogen phosphate, disodium hydrogen phosphate, and  
30     trisodium phosphate.

Examples of polyphosphates and polyphosphonates which can be used include sodium hexametaphosphate, sodium tetrphosphate, hydroxyethanediphosphonic acid, N(-2-carboxyethyl)-1-aminoethane-1,1-diphosphonic acid, N,N-bis-(carboxymethylene)-1-aminoethane-1,1-diphosphonic acid, morpholinomethane-  
5 diphosphonic acid, nitrilotrismethylene-phosphonic acid, ethylenediamine-tetramethylene phosphonic acid, hexamethylenediaminetetramethylene phosphonic acid, 2-phosponobutane-1,2,4-tricarboxylic acid, and 2-carboxyethane-phosphonic acid. Free polyphosphoric acids are also suitable.

- 10 The phosphates, polyphosphates and polyphosphonates are preferably added to the concentrate in an amount ranging from 0.01 to 2.5 mol/litre.

Sodium, potassium and ammonium thiosulfates are particularly suitable as fixing  
agents.

- 15 Other constituents can include aminopolycarboxylic acid, rehalogenating agents, e.g. ammonium bromide, acids and alkalis for pH adjustment, bleaching accelerators, white couplers and buffer substances (see Research Disclosure 37 038, February 1995, pages 107 to 109).

- 20 In particular, the pH ranges from 4 to 9.

In addition, other complexing agents can also be added, individually or in admixture.

- 25 Polycarboxylic acids: e.g. oxalic acid, malonic acid, glutaric acid, adipic acid, suberic acid, fumaric acid, maleic acid, itaconic acid;

- (Poly)hydroxypolycarboxylic acids: e.g. citric acid, glycolic acid, lactic acid, malic  
30 acid, tartaric acid, galactaric acid.

**Example**

1 litre of BX concentrate contains

|   |   |           |
|---|---|-----------|
| 5 | ammonium thiosulfate solution, 57% by weight        | 250 ml    |
|   | ammonium hydrogen sulfite solution, 66% by weight   | 90 ml     |
|   | NH <sub>4</sub> Fe(III)EDTA solution, 48% by weight | 220 ml    |
|   | additives   | see below |
|   | pH  | 5.5       |

10

The following additions were made to the BX concentrates:

BX 1: no additives

BX 2: 40 g/l sodium acetate (0.49 mol/litre)

BX 3: 186 g/l trisodium phosphate dodecahydrate (0.49 mol/litre)

15 BX 4: 50 g/l sodium hexametaphosphate (0.082 mol/litre)

BX 5: 73 ml/l aminotris(methylene)-phosphonic acid, concentration 50% by weight (0.16 mol/litre)

| Storage at 60°C     | Sodium sulfite content [g/l] |      |      |      |      |
|---------------------|------------------------------|------|------|------|------|
| Duration of storage | BX 1                         | BX 2 | BX 3 | BX 4 | BX 5 |
| No storage          | 82.7                         | 82.5 | 82.4 | 82.6 | 82.3 |
| 2 days              | 55.6                         | 56.0 | 65.4 | 64.9 | 65.1 |
| 6 days              | Precipitates of sulfur       |      | 54.0 | 54.2 | 53.8 |

20 The stability of the sulfite is considerably improved by the addition of phosphate, polyphosphate and polyphosphonate.

The BX concentrate according to the invention can be used without disadvantages instead of a conventional, two-part BX concentrate, for example in the standard AP  
 25 94 process for the bleach-fixing of exposed, developed colour paper based on chloride-rich silver halide emulsions.

The BX concentrate according to the invention is particularly suitable for short processing times (CD and BX times ranging from 12 to 35 seconds) and for a colour developer (CD) which contains disulfoethylhydroxylamine (HADS) as an antioxidant.

**Claims**

1. A one-part photographic bleach-fixing agent bath concentrate containing an iron(III) complex salt, a thiosulfate and a sulfite, a disulfite or a sulfinic acid,  
5 characterised in that it additionally contains a phosphate, polyphosphate or polyphosphonate.
2. A one-part bleach-fixing agent bath concentrate according to claim 1,  
10 characterised in that its content of thiosulfate is 0.5 to 25 mol/litre, its content of sulfite is 0.2 to 2 mol/litre and its content of Fe(III) complex salt is 0.1 to 1 mol/litre.
3. A one-part bleach-fixing agent bath concentrate according to claims 1 or 2,  
15 characterised in that its pH is 4 to 9.
4. A one-part bleach-fixing agent bath concentrate according to claims 1 or 2,  
characterised in that its pH is 5 to 6.5.
5. A one-part bleach-fixing agent bath concentrate according to any of claims 1  
20 to 4, characterised in that the amount of phosphate is 0.1 to 2.5 mol/litre.
6. A one-part bleach-fixing agent bath concentrate according to any of claims 1  
25 to 5, characterised in that it additionally contains one or more complexing agents.

**A bleach-fixing agent bath concentrate**

**Abstract**

A one-part photographic bleach-fixing agent bath concentrate containing an iron(III) complex salt, a thiosulfate and a sulfite, a disulfite or a sulfinic acid, remains stable if a phosphate, polyphosphate or polyphosphonate is added thereto.